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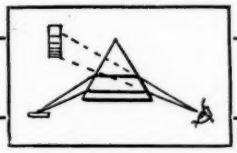

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Errors in Reflectometry

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(Received November 19, 1934)

FOR about fifteen years reflectometers employing small integrating spheres have been in use. In general the test surface has been placed over an opening in the side of the sphere, and has been illuminated by light diffusely reflected from the sphere surface, or by a combination of direct and diffused light. Some of the methods used or proposed, in which light is projected into the sphere through a small hole in the wall, are as follows.

Case I: The test surface, viewed directly by the photometer, receives light diffusely reflected from the sphere walls. By the "substitution method" the test surface is compared with a surface of known reflection-factor.

Case II: The test and standard surfaces are placed over holes close together and are viewed simultaneously by a polarization photometer, or successively by some other type. They receive light diffusely reflected from the sphere surface.

Case III: Direct light is projected onto the sphere wall at a point screened from the test surface. The ratio of the brightness of the test surface to the brightness of the sphere wall at a point unscreened from the directly illuminated spot is assumed to be the reflection factor of the test surface.

Case IV: Direct light is projected first onto the test surface, screened from the part of the sphere wall observed by the photometer, then onto the sphere wall at a point unscreened from the spot observed. The ratio of brightnesses of the observed spot in the first and second conditions gives directly the reflection factor of the test surface.

Several other methods of using the integrating sphere as a reflectometer have been described, but it is not the purpose of this paper to discuss all of them. The four cases outlined above will serve to show the sources of some common errors. These may be briefly summarized as follows.

(A) Errors due to lack of perfect diffusion of light reflected from the sphere walls.

(B) Those due to unequal illumination of test and standard surfaces when the "substitution" method is used.

(C) Loss of light through the necessary holes in the sphere wall.

(D) When the test surface is viewed directly by the photometer, the brightness in the direction of view may depend upon the diffusion characteristics of the test surface and may not be directly proportional to the reflection factor of the surface.

(E) Obstruction of light by the opaque screen, if used.

(F) Errors due to stray light not confined within the concentrated beam projected into the sphere.

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Several of these sources of error have been previously discussed in detail by the author[1, 2, 3] and by others.[4, 5, 6, 7, 8] McNicholas[7] in particular has given a very thorough analysis of the performance of various types of reflectometers, together with a description of a new type instrument.

The definition of reflection factor as adopted by the Illuminating Engineering Society and the American Standards Association is as follows: "Reflection Factor: The reflection factor of a body is the ratio of the light reflected by the body to the incident light. It is the sum of the regular and the diffuse reflection factors." It should be noted, however, that the reflection factor as defined above depends upon the manner in which the body is illuminated. The reflection factor for completely diffused illumination is not always the same as that for directional illumination, but in most cases the difference is small and may be neglected if the light is incident at an angle not greater than 45° from the normal. The effects of the other sources of error outlined above are approximately as follows.

(A) A fundamental assumption in the theory of the integrating sphere as used in photometry and reflectometry is that the sphere surface is a perfect diffuser, and that any elementary area of its surface illuminates all other parts of the the surface equally, without regard to their positions.[9] Let us consider first a sphere with no openings, and with a lamp at the center of the sphere. The illumination of any part of the surface may be analyzed into three components: (a) the light flux received directly from the lamp; (b) the flux contributed by the first reflection of the direct illumination of all other parts of the sphere surface; and (c) the light due to multiple reflections of (b). If the surface is a fairly good diffuser, as is usually the case, the part (c) is quite uniform, and independent of the way in which the direct light is distributed over the sphere surface. In photometry and reflectometry none of the direct light is allowed to fall on the spot observed, hence the departure from perfect diffusion affects only the part (b), since it can be safely assumed that (c) is almost completely diffused.

Let F= the light flux radiated by a lamp in the sphere; A = area of sphere surface; E_d = average direct illumination of sphere walls due to light received directly from the lamp. $E_d = F/A$.

E_t = total illumination of sphere surface; ρ_s = reflection factor of sphere surface; α_s = absorption factor of sphere surface.

$$E_t = E_d[1+\rho_s+\rho_s^2+ \cdots +\rho_s^{(n-1)}]$$
$$= E_d(1-\rho_s^n)/(1-\rho_s). \quad (1)$$

Since n is infinite,

$$E_t = E_d/(1-\rho_s) = E_d/\alpha_s. \quad (2)$$

If the direct light is screened from the spot observed, or if the light is projected into the sphere from outside and illuminates a spot on the sphere wall other than the spot observed by the photometer, the illumination of the spot observed will be

$$F/A\alpha_s - F/A = (F/A)(1-\alpha_s)/\alpha_s = F\rho_s/A\alpha_s. \quad (3)$$

The illumination of this spot by the *first* reflected flux from the sphere wall, the part designated as (b) above, will be $F\rho_s/A$. Hence the ratio of this part (b) to the total illumination of the observed spot will be

$$F\rho_s/A \div F\rho_s/A\alpha_s = \alpha_s. \quad (4)$$

[1] A. H. Taylor, *The Measurement of Diffuse Reflection Factors and a New Absolute Reflectometer*, J. O. S. A. **4**, 9 (1920); Bur. Standards Sci. Pap. No. 391, 1920; Elec. World **76**, 467 (1920). See also discussion of papers at 1919 convention of I. E. S., Trans. I. E. S. **15**, 132 (1920).

[2] A. H. Taylor, *A Simple Portable Instrument for Measuring Reflection and Transmission Factors in Absolute Units*, Trans. I. E. S. **15**, 811 (1920); Bur. Standards Sci. Pap. No. 405, 1921.

[3] A. H. Taylor, *The Measurement of Reflection Factors in the Ultraviolet*, J. O. S. A. **21**, 776 (1931).

[4] C. H. Sharp and W. F. Little, *Measurement of Reflection Factors*, Trans. I. E. S. **15**, 802 (1920).

[5] Enoch Karrer, *Use of the Ulbricht Sphere in Measuring Reflection and Transmission Factors*, Bur. Standards Sci. Pap. No. 415, 1921; J. O. S. A. **5**, 96 (1921).

[6] J. W. T. Walsh, *Note on the Integrating Sphere Reflectometer*, Trans. I. E. S. **18**, 475 (1923).

[7] H. J. McNicholas, *Absolute Methods in Reflectometry*, Bur. Standards J. Research **1**, 29 (1928).

[8] A. C. Hardy and O. W. Pineo, *The Errors Due to Finite Size of Holes and Sample in Integrating Spheres*, J. O. S. A. **21**, 502 (1931).

[9] E. B. Rosa and A. H. Taylor, *Theory, Construction and Use of the Photometric Integrating Sphere*, Bur. Standards Sci. Pap. No. 447, 1922.

Thus it is seen that if α_s is small, i.e., if the reflection factor of the sphere surface is high, errors due to imperfect diffusion of light by the sphere surface would be quite small since such errors would be some small fraction of the first reflected component of the total illumination, i.e., a small fraction of α_s.

(B and C) Hardy and Pineo[8] have derived equations to show the magnitude of the errors introduced in the substitution method of reflectometry (Case I) by the finite size of holes and test object. They find that if the sphere is coated with magnesium oxide (reflection factor 97 percent) and if the holes and the test surface each compose 1 percent of the sphere area, the error may be as large as 25 percent. Usually the test surface composes more than 1 percent of the sphere area, and consequently the error may be even greater than they computed. The error arises from the fact that when the test surface differs in reflection factor from the standard, its illumination by multiply-reflected light is not the same, since the *average* absorption of the sphere, test surface and holes is not the same in the two cases.

(D) In several methods of reflectometry proposed or in use the test surface is placed over an opening of the sphere and is viewed directly by the photometer (Cases I, II and III are examples). It is usually assumed that the brightness of the test surface in the direction of view is proportional to the reflection factor. This assumption was first theoretically attacked by Walsh,[6] who showed that large errors might result from this method of observation. McNicholas[7] found experimentally that some of Walsh's assumptions were incorrect, but that nevertheless large experimental errors could result from observations made in this way, with the direction of view approximately normal to the surface. The present author[2] found that many surfaces, when illuminated normally and viewed at an angle of approximately 50° from the normal, had brightnesses proportional to their reflection factors. However, it is evident that this cannot be the case with all surfaces, e.g., polished black glass, the reflection from which would be entirely specular. McNicholas found that if the illumination of the specimen was totally diffused, the angle of view which gave an "apparent reflectance" the same as the true reflection factor was approximately 55 to 60° from the normal. However, he summarizes the matter thus: "The proper choice of the angle of observation is thus seen to be of prime importance; but, unfortunately, there is no one angle suitable for all samples and apparently no simple correction which may be readily applied to eliminate the effect." He found that with completely diffused illumination and viewing normally to the surface, the errors of measurement ranged from 0 to −56 percent. The greatest errors occurred when measuring specimens having low reflection factors.

From the above discussion, applying especially to relative measurements of reflection factor either by the substitution method or by direct comparisons, it is evident that the experimental errors may be quite large if the arrangement is as outlined in Case I or II, although much lower in Case II than in Case I.

A number of "absolute" methods of reflectometry have been proposed. Case IV represents a type of "absolute" reflectometer proposed by the present author.[2] Many instruments of this type are now in use, hence for convenience in discussing the possible sources of error in this method of reflectometry the actual arrangements and dimensions of one of these will be described.

Fig. 1 is a scale drawing of one of these instruments embodying the latest design. The sphere has a diameter of 4 inches, and the hole over which the test specimen is placed has a diameter of $1\frac{1}{2}$ inches. The test surface composes approximately 3.5 percent of the total area. By means of lenses L_1 and L_2 in the lighting tube T_1 light from a small lamp may be projected onto the test surface. The lighting tube T_1 may be rotated 180° about an axis passing through the center of the sphere to the position T_2. A Macbeth illuminometer, supported by the ring R, has its L-shaped horn, with translucent plate removed, connected to the sphere so as to view a small spot on the sphere wall at P_1 through hole H. A lens in the L-shaped tube of the illuminometer limits the field of view at P_1 to a diameter of approximately 3/16 inch. This spot is screened from the test surface by a small opaque screen S.

When the lighting tube is in the position T_1 the light flux F projected into the sphere must be

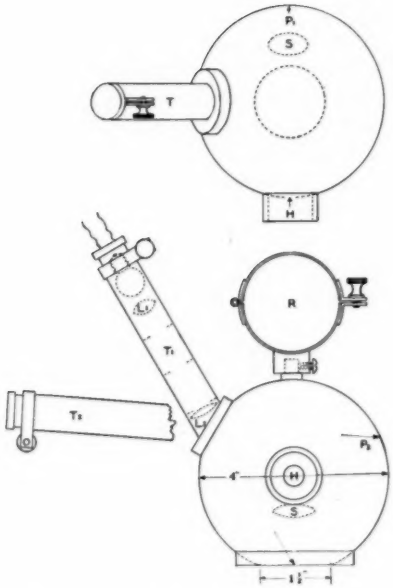

FIG. 1. Arrangement of parts in Taylor "absolute" reflectometer for attachment to Macbeth illuminometer.

reflected once by the test surface and once by the sphere wall before any of it can reach the point P_1. Hence the flux effective in illuminating this point is $\rho_x\rho_s F$, where ρ_x and ρ_s are the reflection factors of the test surface and the sphere surface, respectively. When the lighting tube is in position T_2 the flux F is projected onto the sphere wall at the point P_2, hence the quantity of light effective in illuminating P_1 is $\rho_s F$, since P_2 is not screened from P_1. If we assume perfect diffusion of the light reflected from the sphere wall, the brightness of the spot P_1 will be directly proportional to these values. If A_1, A_2 and A_3 are the areas of the holes, the test surface and the remainder of the sphere, respectively, and α_1, α_2 and α_3 the corresponding absorption factors, the *average* absorption factor would be

$$\alpha=(A_1\alpha_1+A_2\alpha_2+A_3\alpha_3)/(A_1+A_2+A_3). \quad (5)$$

When the lighting tube is in position T_1 and the light is directed toward the test surface, the illumination of P_1 the spot observed, is

$$E_1=\rho_x\rho_s F/\alpha(A_1+A_2+A_3). \quad (6)$$

When it is in position T_2 the illumination of P_1 is

$$E_2=\rho_s F/\alpha(A_1+A_2+A_3). \quad (7)$$

Hence $$E_1/E_2=\rho_x. \quad (8)$$

Thus it is readily seen that the reflectometer is an "absolute" instrument, that no known reflection standard is required, and that the ratio of E_1 to E_2 gives directly the reflection factor of the test surface, without regard to the way in which the light reflected by the test surface is diffused. We will now consider some ways in which the action of an actual reflectometer may depart from these theoretical assumptions.

(A) If the test surface is a diffusely reflecting specimen, the first reflected flux from it will be distributed more or less uniformly over the whole sphere surface (except point P_1) when the lighting tube is pointed directly at it. If the sphere surface is not a perfect diffuser, as assumed in developing the theory, a definite amount of light flux uniformly distributed over it may not illuminate P_1 to the same intensity as an equal amount of light flux concentrated at P_2. In this case the ratio of E_1 to E_2 might not give directly the reflection factor of the test surface.

The author[9] has previously investigated the effect of departures from perfect diffusion upon the errors of integration. Computing the errors arising from imperfect diffusion by the sphere surface, it was found that when the direct light is concentrated in a spot 90 degrees from the spot observed by the photometer the errors are the same in amount as when the direct flux is uniformly distributed over the sphere surface and thus cancel out. Hence, if the direct light flux is to be concentrated in a spot, the most favorable position for this spot is approximately 90° along the circumference from the spot observed by the photometer. It will be seen by Fig. 1 that the spot P_2 is approximately 90° from P_1. Also, if the test surface is a specular reflector such as a mirror, the image of the projected light spot is thrown onto the reflectometer wall at a point approximately 90° from P_1.

(C) We will now consider the effect of light lost through the necessary holes in the sphere. In the reflectometer shown in Fig. 1 the combined area of the two holes through which the light is projected and through which the spot P_1 is

observed is approximately 0.5 percent of the total area. If the test surface is a perfect diffuser, 0.5 percent of the first reflected flux will be lost through these holes and the reflection factor measured will be low by this amount. If the test surface is a mirror, none of the first reflected light is lost through the holes, hence they cause no error. Hence in general the error caused by the holes is probably of the order of 0.3 percent.

(E) The opaque screen S which screens the test surface from P_1 is a necessary part of the reflectometer. It intercepts a part of the first reflected flux, if the test surface is diffusing. In the case of a perfectly diffusing test surface approximately 3 percent of the first reflected flux would be intercepted, and would require an additional reflection from S before it could reach the sphere wall at points unscreened from P_1. If ρ_s is 90 percent, the amount absorbed by the screen would be 0.3 percent, and most of the remaining 2.7 percent would be reflected onto the sphere and be effective in illuminating P_1. However, a small part of this would be reflected back onto the test surface, causing additional absorption. The screen error is a maximum when the test surface is a perfect diffuser, but it probably would not exceed 0.5 percent in any case. When the sphere and screen are smoked with magnesium oxide ($\rho_s = 97$ percent) the error would be correspondingly reduced.

When the test surface is a specular reflector none of the first reflected flux strikes the screen S, hence it causes no error. Since most surfaces are imperfect diffusers, the screen error probably does not usually exceed 0.3 percent.

(F) The source of the greatest error encountered in the use of the reflectometer shown in Fig. 1 is probably stray light from the lighting tube. Unless all the light projected into the sphere falls on the test surface when the tube is in position T_1 the reflection factor as measured will usually be too high. It is almost impossible to avoid a small amount of stray light, caused by dust particles on lens L_2 and reflections from diaphrams, etc. in the tube. If the lamp is properly focused, the amount of stray light is small and introduces very little error if the test surface reflects more than 25 percent. Its greatest effect is encountered when measuring surfaces having very low reflection factors. Apparently this effect accounts for most of the differences found by McNicholas[7] between measurements by his reflectometer and by two Taylor reflectometers. Fortunately, a correction for stray light can be easily determined and applied.

Let F = total direct light flux entering sphere; XF = the fraction of the direct light flux which is scattered, and reaches the sphere wall without reflection from the test surface. ρ_x = true reflection factor of test surface.

Then

$$E_1/E_2 = \frac{(1-X)\rho_x F + XF}{F} = (1-X)\rho_x + X = \text{reflection factor as measured} = R; \quad \therefore \rho_x = (R-X)/(1-X).$$

X may be measured by leaving the reflectometer hole (over which the test surface is usually placed) open, and measuring the ratio $E_1 \div E_2$, the work being done in a dark room.

In using this reflectometer care must be taken to place the screen S so that the spot observed by the photometer is completely screened from the test surface. If this is done and the stray light correction applied, the reflection factor determined is probably correct to within approximately one percent. However, it should be definitely understood that the value measured is for the direct light incident approximately 30° from the normal to the surface. Also, if the test surface is colored, the reflection factor measured is for light from a small tungsten lamp, color temperature approximately 2400 to 2500° K, and would be somewhat different if daylight was the light source.

Summary

Some of the commoner sources of error in reflectometry as now practiced have been analyzed and their effects computed. Corrections can be made for some of these, but others are indeterminable and should be avoided.

In the "substitution" method of reflectometry, where the test and standard surfaces are placed successively over a single opening in the reflectometer sphere and viewed directly by the photometer, the error may be as great as 25 percent if the holes and test sample each occupy one

percent of the total area. Since the opening for the test sample is usually larger than this, the error may be even greater than 25 percent.

Lack of perfect diffusion of the light reflected by the sphere wall may cause an error, but this error will be quite small if the reflection factor of the sphere surface is 90 percent or greater. The most favorable position for a concentrated spot of light projected onto the sphere wall is approximately 90° along the circumference from the spot viewed by the photometer.

Loss of light through the necessary holes in the Taylor absolute reflectometer,[2] which have an area of approximately 0.5 percent of the total area, can cause a maximum error of 0.5 percent if the surface is a perfect diffuser, but no error is caused by the holes if the test surface is a mirror. Most surfaces give results intermediate between these, probably about 0.3 percent.

When the test surface is viewed directly by the photometer, at an angle near the normal, the error in the measured reflection factor may be quite large. McNicholas[7] found errors as large as 56 percent under this condition. The most favorable angle of view is approximately 55 to 60° from the normal, but the correct angle is not the same for all surfaces.

In the Taylor absolute reflectometer the opaque screen absorbs approximately 0.3 percent of the first-reflected flux from the test surface if it is a perfect diffuser and none if it is a mirror (assuming the reflection factor of the sphere surface to be 90 percent). Multiple reflections between the screen and test surface may raise the error of measurement to approximately 0.5 percent when measuring specimens having low reflection factors.

With this reflectometer stray light not confined to the projected beam may give results which are too high when measuring surfaces having low reflection factors. However the proper correction can be easily measured and applied to the results.

Luminescence of Thorium Oxide Activated by Rare Earths. Optimum Concentration for Different Sources of Excitation

FRANCES G. WICK AND CHARLOTTE G. THROOP, *Vassar College*

(Received November 26, 1934)

Three sets of specimens were prepared in which thorium oxide contained as activators praseodymium, samarium and terbium in concentrations varying by known amounts. The specimens activated by praseodymium varied from 1 atom of praseodymium in 100 molecules of thorium oxide to 1 atom in 100,000 molecules; those activated by samarium from 1 atom in 15.5 molecules to 1 atom in 2000 molecules: those activated by terbium from 1 atom in 10 molecules to 1 atom in 40,000 molecules. The intensity of luminescence of specimens in each set was measured and the concentration of greatest brightness, the optimum concentration, determined for each of the following sources of excitation: cathode rays, ultraviolet light and hydrogen flame. The results show that the optimum concentration is different for each of the sources of excitation used. In all cases the concentration required for the optimum under cathode rays is less than that for the other methods of excitation used.

LUMINESCENT solids are, in general, mixtures in which a small amount of some substance, the activator, is intimately associated with a relatively large amount of another substance, the diluent. Minute traces of a certain activator in a given compound will produce a luminescent material. As the percentage of activator increases the intensity of luminescence under a given mode of excitation quickly increases to a maximum point called the "optimum"[1] then steadily decreases. Kowalski[2] and Garnier have shown that the "optimum" for a given luminescent substance depends upon the method of excitation. They found that the optimum concentration of samarium in calcium sulphate is 1 part to 125 to 400 under cathode-ray excitation and 1 part to 4000 under ultraviolet light.

The experiments described in this paper were undertaken for the purpose of making comparisons of the "optima" under different sources of excitation. Three sets of specimens of thorium oxide activated, respectively, by praseodymium, samarium and terbium were prepared. The specimens were excited by the hydrogen flame, by cathode rays, by ultraviolet light and by x-rays. The intensity of luminescence of the different concentrations excited by each of these sources was measured by means of a Leeds and Northrup optical pyrometer with a filter in the eyepiece giving an approximate color match. From the current through the filament of the pyrometer lamp when it matched the specimen in brightness the candle-power per square centimeter of the specimen under observation was determined from the data of Forsythe.[3]

The specimens were prepared under identical conditions as follows: A measured volume of a gram-atom solution of a rare earth compound—usually the nitrate—was put into a weighed amount of thorium nitrate and the mixture was heated from below by a Bunsen burner until the nitrate had been converted into thorium oxide. The number of molecules of thorium oxide to one atom of rare earth could easily be computed. The specimen thus prepared was heated to a temperature of 650° C, kept at this temperature for 15 minutes then slowly cooled to room temperature. Since any variation in heating causes a difference in the intensity of luminescence it was important that all the specimens be subjected to exactly the same heat treatment. A very satisfactory electric furnace for this purpose suggested by E. L. Nichols was used. Two conical glocoils, *A* and *B*, Fig. 1, were mounted with the bases of the heating coils in contact. An inverted crucible lid *C* mounted on top of a crucible *D* contained the specimen. A chromel-alumel thermojunction *E* was imbedded in the specimen. This method of heating was very satisfactory since with a given current at a definite voltage a given temperature could be produced and maintained as shown by the thermojunction.

[1] H. F. V. Little, *Textbook of Inorganic Chemistry*, Vol. IV, p. 297.

[2] Kowalski and Garnier, Comptes rendus **145**, 391 (1909).

[3] Forsythe, J. O. S. A. **16**, 307 (1928).

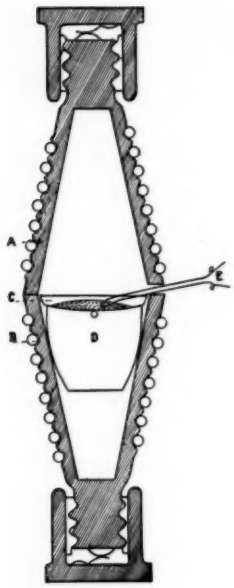

FIG. 1.

SOURCES OF EXCITATION

For hydrogen flame excitation the specimens were placed in a thin layer upon the end face of a cylindrical copper block large enough to hold a number of concentrations at the same time. The block was heated from below as described by Nichols and Howes[4] and the temperature of the copper surface was determined by a copper-platinum thermojunction pounded into the copper face. The specimens were brought alternately within the oxidizing part of a small hydrogen flame and the intensity of a definite temperature crest in the different concentrations was measured. Various materials activated by rare earths are known[4, 5, 6] to show marked temperature crests at which brightness maxima occur.

Under cathode-ray excitation thorium oxide activated by rare earths is strongly luminescent. With the method of previous experiments[7] the specimens to be compared were mounted simultaneously upon an aluminum holder 4 cm square in a tube having a ground glass joint and a diameter of 6 cm. The powdered specimens were mixed with amyl acetate and painted on the holder in strips about 4 mm wide. The tube was exhausted by a large hyvac oil pump kept running during the observations since the specimens emitted gas upon bombardment. As a source of high voltage a General Electric testing set was used in which the rectifying units were kenetrons. In series with the tube on the high voltage side of the line was placed the secondary of an induction coil. By adjustable resistances and proper vacuum control reasonably constant conditions could be maintained as indicated by a voltmeter and an ammeter. Each specimen was bombarded at an angle of about 45 degrees for about 30 seconds while an observation of brightness was made, then, with the discharge off, the pump was run for a definite time to hold the vacuum at a definite condition as indicated by the voltmeter and ammeter before the observation of the next specimen. Repeated observations checked in such a way as to indicate constant conditions.

Under ultraviolet excitation the luminescence is faint but measurable. Light from an iron spark run on the secondary of an Andrews transformer was dispersed by an ultraviolet illuminator made of two quartz lenses and a quartz prism the calibration of which was kindly furnished by D. T. Wilber. The region of the ultraviolet effective for excitation was different for the various rare earth activators.

X-rays from a molybdenum target tube running at 80 kv and 4 m.a. were thrown upon the specimens through one thickness of black paper at a distance of a few cm. A variation in intensity with concentration was observable and it was possible to pick out the optimum but the intensity was too faint for measurement. Through the kindness of Dr. H. C. Rentschler of the Westinghouse Lamp Company the specimens were also exposed to x-rays from a Granz tube at 40 kv and 25 m.a. and also to rays from a tube

[4] Nichols and Howes, J. O. S. A. **22**, 170 (1932).
[5] Nichols and Boardman, J. O. S. A. **20**, 115 (1930).
[6] Nichols and Wick, J. O. S. A. **22**, 357 (1932).
[7] Wick, Phys. Rev. **24**, 272 (1924).

with a line focus running at 70 kv and 100 m.a. The brightness was not, in any case, sufficient for measurement.

Terbium in Thorium Oxide

The luminescence of thorium oxide activated by terbium is green in color matched by a Wratten No. 44 filter used in the eyepiece of the optical pyrometer. Specimens varying from 1 atom of terbium in 31.25 molecules of thorium oxide to 1 atom in 40,000 were prepared to cover the optima for all methods of excitation.

Under hydrogen flame excitation these specimens show a temperature crest at about 250° C. In order to get the intensity at this crest the copper block upon which the specimens were heated was brought to a temperature of 350° C. As it cooled the brightness of the different specimens was measured alternately at various temperatures until the block had cooled to 125° C. A temperature-brightness curve was plotted for each concentration and from these curves the brightness of the crest for each concentration was obtained as given in Table I.

Table I. *Terbium in thorium oxide.*

Concentration molecules ThO_2 to 1 atom Tb	Brightness in cp. per cm²		
	H flame excitation	Cathode-ray excitation	Ultraviolet excitation
10			0.0005370
31.25	0.0166		.001622
62.5	.0324	0.001349	.0020214
250	.0261	.002455	.0009179
500	.0260	.002645	.0003981
1000	.01065	.001864	.0003203
3333.3		.0006185	.0001733
20,000			
40,000		.0001950	

Curve 1, Fig. 2 shows the brightness of the various concentrations plotted against the concentration expressed in molecules of thorium oxide per atom of terbium.

Under cathode-ray excitation, observations were made upon specimens varying from 1 atom of terbium in 62.5 molecules of thorium oxide to 1 atom in 40,000 molecules keeping the voltage on the tube 4800 and the current 0.5 m.a. The results are shown in Table I and in curve II, Fig. 2. Another set of observations at a voltage of 4800 and a current of 0.2 m.a. gave the same optimum.

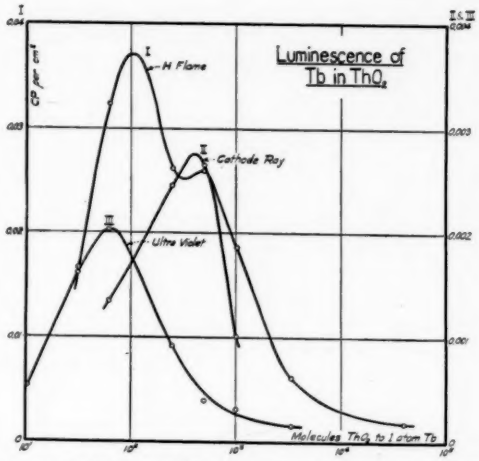

Fig. 2. Brightness of luminescence of different concentrations of terbium in thorium oxide. Curve I. Hydrogen flame excitation; curve II. Cathode-ray excitation; curve III. Ultraviolet excitation.

Under ultraviolet excitation the intensity of luminescence was very low. The region of strongest excitation was between 2500 and 2900A. Measurements were made of specimens varying from 1 atom of terbium in 10 molecules of thorium oxide to 1 atom in 333 molecules. The results are shown in Table I and in curve III, Fig. 2. Specimens from 1 atom in 20,000 to 1 atom in 40,000 molecules were observed to have a purplish color quite different from the green color of the more concentrated specimens. Urbain observed a color change with change in concentration of activator under cathode-ray excitation. He makes the statement, "The general rule may be stated that the most refrangible rays are at their maximum for smaller percentages of activator than the less refrangible rays. Hence, as the percentage of activator changes from zero upward the changes observed in the color of phosphorescence occur from blue to red along the spectrum." The luminescence of material activated by rare earths consists of bands which, according to Urbain, vary independently with the percentage of activator.

A comparison of the curves in Fig. 2 shows that the highest concentration of terbium is required to produce the optimum under ultraviolet excitation and the lowest under cathode rays.

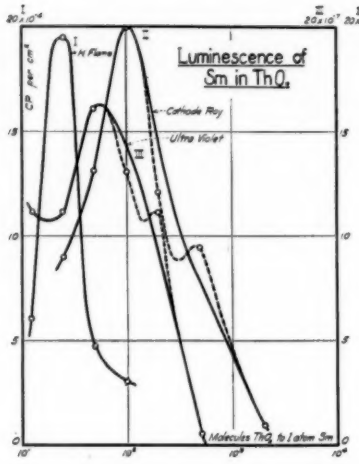

FIG. 3. Brightness of luminescence of different concentrations of samarium in thorium oxide. Curve I. Hydrogen flame excitation; curve II. Cathode-ray excitation; curve III. Ultraviolet excitation.

SAMARIUM IN THORIUM OXIDE

The luminescence of thorium oxide activated by samarium is reddish in color, approximately matched by Wratten F, No. 29 filter. Concentrations varying from 1 atom of samarium in 12.5 molecules of thorium oxide to 1 atom in 2000 were prepared.

Under hydrogen flame excitation observations were made to determine the brightness of different concentrations at a temperature crest at about 640° C. At this temperature the copper block is cherry red and the observations were difficult and not altogether satisfactory. The results are shown in Table II and in curve 1, Fig. 3.

Under cathode rays specimens were observed varying in concentration from 1 atom of samarium in 25 molecules of thorium oxide to 1 atom in 2000 molecules. The voltage on the tube was 4000 and the current through it 0.8 m.a. The results are shown in Table II and in curve II of Fig. 3.

Under ultraviolet excitation the luminescence is relatively strong and orange-red in color. The region of greatest excitation is about 2200A, the intensity diminishing rapidly as the specimen is moved toward the shorter wavelengths and more gradually as it is moved toward the longer wavelengths. The results are shown in Table II and in curve III, Fig. 3.

Under x-rays the luminescence is too dim for even an approximate determination of the optimum.

From a comparison of the curves in Fig. 3 it will be observed that the highest concentration of samarium is required for the optimum under hydrogen flame excitation, the lowest under cathode rays.

TABLE II. *Samarium in thorium oxide.*

Concentration molecules ThO_2 to 1 atom Tb	Brightness in cp. per cm²		
	H flame excitation	Cathode-ray excitation	Ultraviolet excitation
12.5	0.00060255		0.000001122
25	.001950	0.00009003	.000001122
50	.0004786	.0001312	.000001622
100	.0003020	.0001999	.000001322
200		.0001210	.000001122
500		.00009455	.0000005248
2000		.000009333	

PRASEODYMIUM IN THORIUM OXIDE

The luminescence of thorium oxide activated by terbium is red in color matched by a Wratten F No. 29 filter. Under the hydrogen flame, measurements were made upon a temperature crest between 230° and 250° C in concentrations varying from 1 atom of praseodymium in 100 molecules of thorium oxide to 1 atom in 800. Difficulty was encountered in these observations because of the fact that the intensity of luminescence varied greatly with the part of the hydrogen flame to which the specimen was exposed. It was found best to support the burner vertically and use the tip of the flame for excita-

TABLE III. *Praseodymium in thorium oxide.*

Concentration molecules ThO_2 to 1 atom Tb	Brightness in cp. per cm²		
	H flame excitation	Cathode-ray excitation	Ultraviolet excitation
100	0.00076	0.00003467	0.000002291
200	.00142	.00004467	.000004365
400	.00133	.00008338	.000007079
800	.00106	.00006894	.000003800
2000			.000002291
4000		.00003467	.000001622
40,000		.000009333	
400,000		.000004898	

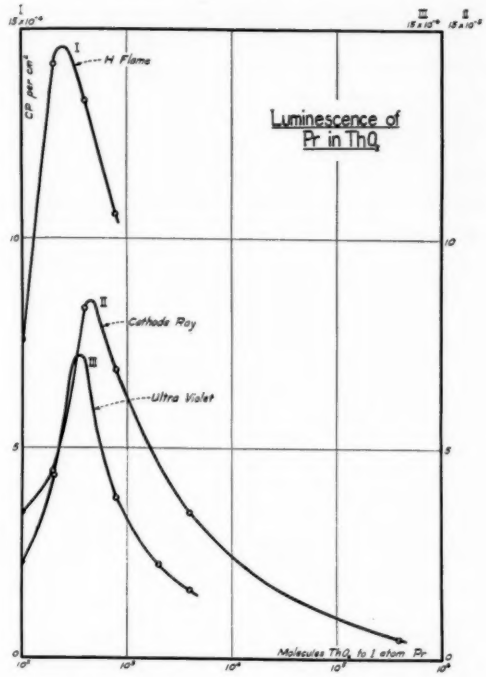

FIG. 4. Brightness of luminescence of different concentrations of praseodymium in thorium oxide. Curve I. Hydrogen flame excitation; curve II. Cathode-ray excitation; curve III. Ultraviolet excitation.

tion. The results are shown in Table III and in curve I, Fig. 4.

Under cathode-ray excitation specimens were observed varying from 1 atom of prasedoymium in 100 molecules of thorium oxide to 1 atom in 400,000. There is a gradual color change from red at the concentrated end of the series to a more bluish color at the dilute end. This is in agreement with the observations of Urbain. The results are shown in Table III and in curve II, Fig. 4.

Under ultraviolet excitation measurements were made upon specimens varying from 1 atom of praseodymium in 100 molecules of thorium oxide to 1 atom in 4000. Filter Wratton No. 27, stage red, was used in the eyepiece of the pyrometer since the red filter used in the hydrogen flame and cathode-ray excitation was found to reduce the intensity too much. The region of greatest excitation was between 2900 and 3000A. The results are shown in Table III and curve III, Fig. 4.

TABLE IV. *Optimum concentrations of different rare earths in thorium oxide. Taken from curves in Figs. 1, 2 and 3.*

	Optimum in molecules ThO_2 per atom			
Activator	Under cathode ray	Under hydrogen flame	Under ultra-violet light	X-rays
Terbium	389	158.5	69.18 Exciting wavelengths 2500–2900A	62.5
Samarium	69.18	23.44	48.98 Exciting wavelength 2200A	
Praseodymium	489.8	263	346.7 Exciting wavelengths 2900–3000A	200 to 400

These specimens were feebly excited by x-rays the optimum concentration appearing to be between 1 atom of praseodymium in 200 and 1 atom in 400 molecules of thorium oxide.

Table IV shows the optimum concentrations under different forms of excitation for each of the rare earths used as activators, taken from Figs. 2, 3 and 4. For terbium in thorium oxide the optimum under cathode rays is lowest in concentration and under ultraviolet light highest. Tentative observations under x-rays show a still higher concentration for the optimum. For samarium the optimum concentration under cathode rays is least and under the hydrogen flame greatest. There are indications of secondary maxima. For praseodymium the optimum concentration under cathode rays is least and under ultraviolet light greatest.

SUMMARY

Specimens of thorium oxide activated by rare earths show different optima for different methods of excitation.

The concentration required for the optimum under cathode rays is, in all cases, less than that for the same activator under ultraviolet light. This is not in agreement with the work of Kowalski and Garnier[2] upon samarium in calcium sulphide. The optimum found by them for this material is less for ultraviolet light than for cathode-ray excitation. The variation in the position of the optimum under the hydrogen flame

relative to the other excitations may be accounted for by the fact that observations under the hydrogen flame are difficult to make and the results subject to error because of unsteadiness of conditions.

The region of the ultraviolet most effective in producing luminescence varies with the different activators. The highest concentration of rare earth is required for optimum for the activator which requires the highest frequency of exciting light.

This work was done in The Laboratory of Physics at Cornell University. The authors acknowledge gratefully the hospitality of the Department of Physics at Cornell and wish to express their sincere appreciation of the interest and suggestions of Professor E. I. Nichols during the whole course of the work.

Resolution Threshold of the Continuously Open Eye

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AMONG the known consequences of keeping the eye continuously open for prolonged periods are discomfort, drying of the corneal surface, lacrimation, increased tendency to blink, and retinal adaptation. The effect on acuity, however, does not appear to have been investigated before and there are other reasons for investigating it. Results might be helpful to workers or observers in exacting visual situations in deciding whether to wink rapidly or stare unblinkingly when trying to resolve detail. Ophthalmologists are interested in effects of protracted exposure of the living cornea for such exposure may be convenient in examinations or necessary during operations. Sufficient changes in the optical properties of the cornea or in retinal sensitivity would be reflected in acuity measurements.

An unfulfilled requirement of many adaptation experiments is to stimulate a limited retinal area with a constant stimulus for a considerable and strictly continuous duration. Conditions to be met are an unobstructed pupil and freedom from distracting discomfort, both for a sufficient duration. Besides measuring the resolution threshold, the present experiments aim to be indicative of the adequacy with which the above conditions can be met when a particular technique is employed for keeping the eye continuously open.

LID-RESTRAINING DEVICE

The eye was held open by means of a small silver bar with a somewhat spoon-shaped end for keeping the upper lid clear of the pupil. With the aid of a light screw-and-lever mechanism attached to reinforced spectacle frames, the bar could be adjusted within the three spatial dimensions and swung quickly in or out of position. Some of the details of this restraining device had been redesigned and it was more comfortable than when originally described.[1] The weight of the mechanism as a whole had been substantially reduced and while the spoon-like end remained the same in length and width, it was only two-thirds as thick, more rounded around the edge, and less curved as viewed from above or below. Spring ear-pieces, fibre forehead braces, and a broad conforming nose-piece kept the device in position with comparative comfort.

Fig. 1 shows the form of the restraining bar and also the correct adjustment. This picture was taken from below while the subject was looking ahead at a fixation point in the normal position. The spoon clears the globe by somewhat less than 1 mm and lightly supports the lid at the roots of the lashes. It is adjusted high enough above the pupil to avoid interference with entering light. The eye is widely opened when the bar is brought into position to assure getting all the lashes above it. The spoon is then moved close enough to the cornea to prevent winks of moderate force from pushing the lid down behind it. After a stop-screw has been set to define the adjustment, the bar may be swung away from the eye and only returned to position for actual

FIG. 1. Lid-restraining bar in position.

[1] S. M. Newhall, *The Control of Eyelid Movements in Visual Experiments*, Am. J. Psych. **44**, 562 (1932).

experimentation.[2]

The restrainer was demonstrated and each subject practiced at odd moments over a period of several days in adjusting it to his own eye. After some familiarity and habituation had been gained in this way, several time trials were made. In each trial the bar was to be left in position as long as was "not too uncomfortable" but never longer than 30 minutes. The subject was instructed to look steadily at a fixation mark a few feet away with no effort to refrain from natural blinking. Table I below gives the mean of the best three trials for each subject.

TABLE I.

Subject number	1	2	3	4	5	6
Mean duration in min.	30.0	34.0	30.0	23.7	14.1	10.7

Several factors were reported which obviously operated to bring trials to a close. Apart from the time limit itself, these included a few unavoidable interruptions external to the experiment, pain or discomfort infrequently accompanied by marked lacrimation, unpleasantness as distinguished from discomfort, slipping of the lid behind the restraining bar. No untoward after-effects were reported or observed.

The results of these time trials suggest that the duration and comfort requirements of many adaptation experiments can be satisfied provided only that the restraint of the lid does not entail disturbing change in the refractive media. Gathering of transient film or irregularities at the corneal surface might produce visual effects which could be confused with others of retinal origin. The acuity series to be described aimed to differentiate this physical factor. The durations used in those series were selected with reference to the time trials above.

TEST OBJECT

Acuity was measured by means of the Ives crossed grating test object.[3] The mean field brightness was held nearly constant at 3.98 ml.[4] Since this instrument produces bands which can be varied continuously from clearly visible striation to below the point of mergence or apparent homogeneity, the just perceptible width was psychophysically determinable. The limiting method was employed. Then the absolute width W of the threshold bands was calculated by Ives' formula.[5] Present results are expressed in terms of W and W-ratios. The value of W with the subject at a fixed distance from the test surface is taken as the measure of the resolution threshold. During experimentation the subject sat in a darkened booth with his dominant eye in position and observed monocularly. A sliding screen in the wall of the booth was used for exposing the test surface.

Two experiments were performed on the effect of artificial lid restraint on acuity, the first to discover what measurable effect there might be after the subject had worn the lid holder as long as feasible, and the second to trace the course of possible variation in acuity while the subject was wearing the holder.

EFFECT ON ACUITY OF PROLONGED LID-RESTRAINT

The procedure of this experiment included three control series during which the subject observed without lid-restraint. Two of these series preceded the period of restraint. They were designed not only to provide a baseline but also to indicate the order of reliability of the measurements. If, because of practice effect, the second series did not check fairly well with the first, the latter was thrown out and an extra control series was run. The final control series succeeded the period of restraint after the lapse of a short recovery interval. The experimental or restraint series commenced after the subject had worn the holder for either 10 or 20 minutes and was completed while he was still wearing it. During this period the eye was continuously open. In the few

[2] The lid-holder was found to be unsuited to two individuals who were going to participate in the experiment. In case of one the lashes were very long, even close to the external canthus; and this individual was unable to open his eyes widely. For those reasons it was found impossible to get the bar below all the lashes; on the contrary, some of them would be invariably forced against the cornea. The eye of the other potential subject was too deep-set by about 1/4 in. to get the spoon in the correct position.

[3] H. E. Ives, *A Visual Acuity Test Object*, Elec. World 55, 939 (1910).

[4] The writer is indebted to Dr. K. W. Spence whose acuity set-up was made available for this study during an interval in infra-human primate experimentation.

[5] The formula is, $W = w/2(\sin \frac{1}{2}\theta)$, in which the acute angle, θ, which the two systems of rulings make with each other is read from the instrument scale, and the constant w is the width of the rulings, i.e., 1/480 in.

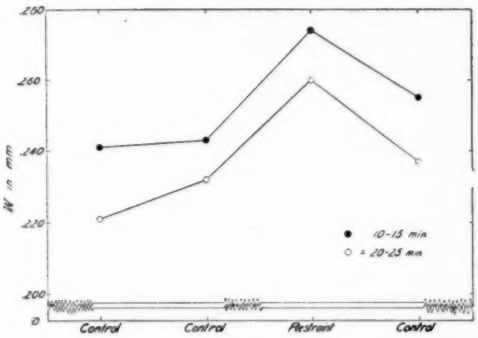


FIG. 2. Resolution thresholds with and without artificial lid-restraint.

instances in which the lid slipped from the restrainer before the measurements could be completed the results were not accepted and the observations were repeated. Since a series required about 5 min., the total period of restraint was either about 15 or 25 min. Before each series there was a period for rest and adaptation. A complete session lasted about 75 min. Within a few days the entire experiment was repeated as a test of consistency.

The procedural sequence in any session may be summarized as follows: (1) preliminary trials, (2) 5 min. dark adaptation, (3) series of 10 control trials, (4) 5 min. dark adaptation, (5) series of 10 control trials, (6) lid-restraint for approximately 15 or 25 min. depending on the subject's performance in the time trials, (7) 5 min. dark adaptation during the next to the last 5 min. of lid-restraint, (8) series of 10 experimental trials, during the last 5 min. of lid-restraint, (9) 5 min. dark adaptation without restraint, (10) series of 10 control trials.

The results of this experiment are plotted as Fig. 2 with resolution threshold W as a function of restraint or non-restraint. In case of half the subjects—those represented by solid circles—restraint was for approximately 15 min., while in case of the others it was for 25 min. Each plotted point is the mean of a total of 60 threshold determinations from three subjects.

Restraint is seen to be accompanied by a definitely higher threshold even though the control measurements after restraint are somewhat higher than before. Though perhaps not significant, the fact seems noteworthy that the mean thresholds for the 15 min. group were *all* higher than for the 25 min. group. The former not only experienced greater difficulty in keeping the eyes open continuously but also evidenced less acuity.

VARIATION IN ACUITY DURING LID-RESTRAINT

Evidence for a rise in threshold having been adduced, it next seemed well to trace the course of variation with the passage of time; for rate of change would presumably be more illuminating than mere fact of change. Accordingly, threshold measurements were now taken every minute throughout the period of restraint or non-restraint as the case might be.

The procedural sequence was briefly as follows: (1) light adaptation, (2) 10 or 20 min. without restraint and with a pair of acuity measurements every minute, (3) 10 min. rest in light, (4) 10 or 20 min. with restraint and with a pair of acuity measurements every minute. In a second session the above procedure was repeated exactly except for temporal reversal of the control and experimental trials (to avoid time error).

The results are shown in Figs. 3 and 4. In either figure, the ordinate represents the ratio of the resolution threshold with restraint to the resolution threshold without restraint, while the baseline represents minutes of time. Values above unity indicate higher thresholds with restraint than without it. Each plotted point signifies the mean of 6 determinations with restraint as related to 6 corresponding determinations with-

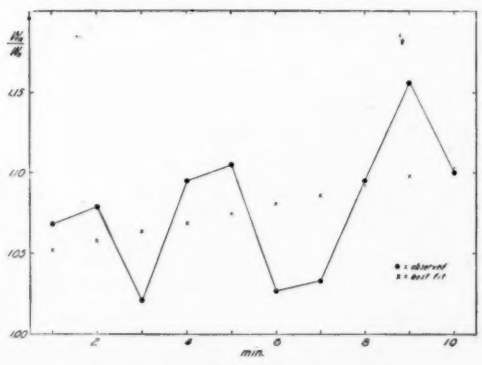


FIG. 3. Resolution threshold with restraint relative to normal threshold, during a period of 10 minutes.

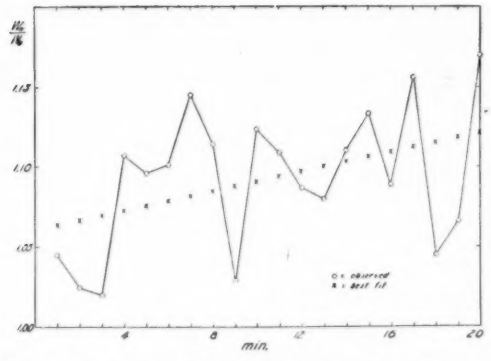
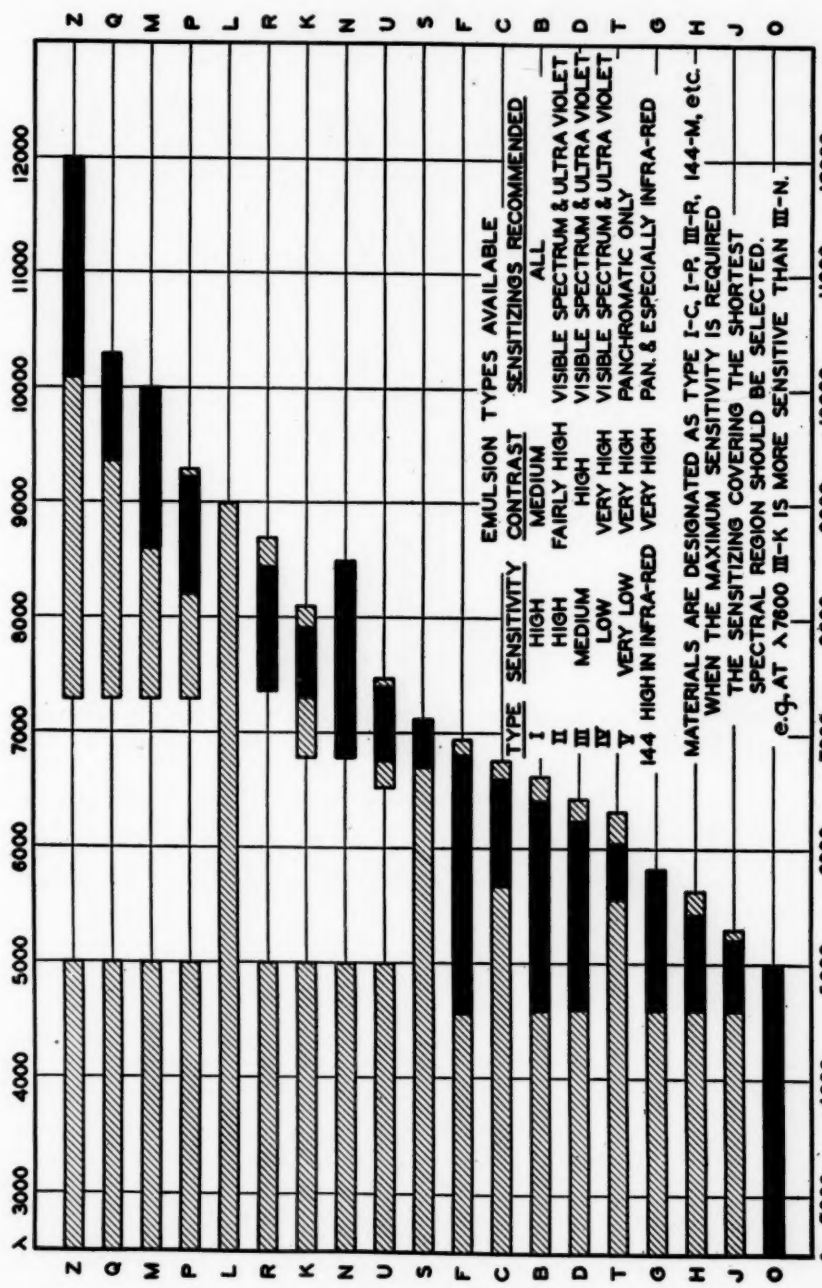


FIG. 4. Resolution threshold with restraint relative to normal threshold, during a period of 20 minutes.

out. Though the variability is high and irregular, the line of least squares is seen to slope upward indicating a tendency to progressive rise in the resolution threshold. Further, the fact that neither curve starts at unity indicates a relatively sudden rise in the threshold due directly or indirectly to lid-restraint.

INTERPRETATION

When the eye was kept continuously open with a mechanical lid-holder there occurred, (1) a relatively sudden rise, of the order of 10 percent, in the resolution threshold followed by a less rapid return following restraint, and (2) a relatively slow rise, of the order of 5 percent, in the threshold during the course of restraint. Because of the controls employed, neither of these changes would seem essentially due to retinal change. Furthermore, they would seem to be too small to confuse results in adaptation experiments. For slight reduction in definition does not interfere with areal judgments of brightness or chromaticity. Probably, therefore, mechanical lid-restraint is an adequate technique for keeping the eye open during a period of minutes.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Z Q M P L R K N U S F C B D T G H J O
EMULSION TYPES AVAILABLE
TYPE SENSITIVITY CONTRAST SENSITIZINGS RECOMMENDED
I HIGH MEDIUM ALL
II HIGH FAIRLY HIGH VISIBLE SPECTRUM & ULTRA VIOLET
III MEDIUM HIGH VISIBLE SPECTRUM & ULTRA VIOLET
IV LOW VERY HIGH VISIBLE SPECTRUM & ULTRA VIOLET
V VERY LOW VERY HIGH PANCHROMATIC ONLY
144 HIGH IN INFRA-RED VERY HIGH PAN. & ESPECIALLY INFRA-RED
MATERIALS ARE DESIGNATED AS TYPE I-C, I-P, III-R, 144-M, etc.
WHEN THE MAXIMUM SENSITIVITY IS REQUIRED
THE SENSITIZING COVERING THE SHORTEST
SPECTRAL REGION SHOULD BE SELECTED.
e.g. AT λ 7600 III-K IS MORE SENSITIVE THAN III-N.

FIG. 3. Diagram of spectral sensitivity regions of spectroscopic plates.